QUASI-ELASTIC LIGHT SCATTERING STUDY OF WATER SOLUBLE POLYMERS

FINAL REPORT

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by

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In this report we will present all the results which have been determined during the course of this two year investigation of water soluble flocculants and the nature of the flocculation process. Each of the following sections corresponds to an obective stated in the original contract proposal or in the proposal for the second phase of the study. We have sincerely enjoyed this investigation and the collaborative nature of our discussions with the scientific authority, Dr. Kirk Michaelian, of the Coal Research Laboratory in Devon, Alberta and with his colleagues, especially Dr. W Freisen.

A) VERIFICATION OF THE ACCURACY AND REPRODUCIBILITY OF THE QELS TECHNIQUE USING SIZE STANDARDS SUCH AS LATEX SPHERES, AND COMPARISON OF THESE RESULTS WITH THOSE OBTAINED USING COMPLEMENTARY TECHNIQUES AT CRL, EDMONTON.

The use of quasi-elastic light scattering (QELS) for particle size analysis is now well established. Studies on latex emulsions, clay fines and coal fines have been performed with significant success in each case. So long as the scattering particles are generally spherical in shape the collection and analysis of data is straight forward. The best scattering angle for these studies is ninety degrees and the best analysis procedure for routine studies is the cumulants method. A program called 'POLY' has been supplied to the Coal Research Laboratory which can perform this analysis on their data. The concentration requirements on the sample are also simple; generally one wants to have as high a concentration of particles as possible without causing any multiple scattering. If multiple scattering occurs then the laser beam through the sample is no longer a clean pencil of light, but becomes diffuse. If experiments are performed on

samples which are multiple scattering then the particle size results will be smaller than the true value. There is no penalty for having lower concentrations of particles in the sample other than lower concentrations yield lower scattered intensities and experiments may take longer to perform. The only exception is if particle concentrations are extremely low such that one has only a few (<10) particles in the scattering volume at any time. In this case one introduces number fluctuations into the dynamics of the scattered light with the result that measured particle sizes would be larger than the proper value. Operationally the optimum concentration is achieved when the count rate yields one count per time bin on the average. Thus if one sees a nice decay on the correlator using a bin time of say 100 microseconds then the optimum count rate is 10000 counts per second. If one is using the cumulants method of analysis then the choice of experimental time depends on the amount of information desired. Operating at the optimum count rate as defined above, the average particle size may be obtained to about 5% after a collection time of about 1000 times the correlation time. The correlation time is the delay time required for the experimental intensity autocorrelation function to fall to 1/e of its t=0 value. If one desires the mean size to about 2% and the width of the distribution to about 15% then a collection time of about 10000 correlation times is required. These same rules of thumb should apply to the sizing of any particulate systems, including oil in water micelles.

We have also developed a more sophisticated analysis procedure called exponential sampling which allows determination of the complete particle distribution. Figure (1) shows such a distribution for latex spheres and Figure (2) shows similar results from a suspension of coal fines. While

FIGURE 1. Size Distribution: Histogram plot, using the exponential sampling technique (equation 12), for polystyrene spherical particles. This analysis yields an average radius of 0.173 ± 0.1 μm, while an average value of 0.130 ± 0.05 μm was obtained from electron microscopy. The particles were suspended in water as 0.001 % solids.

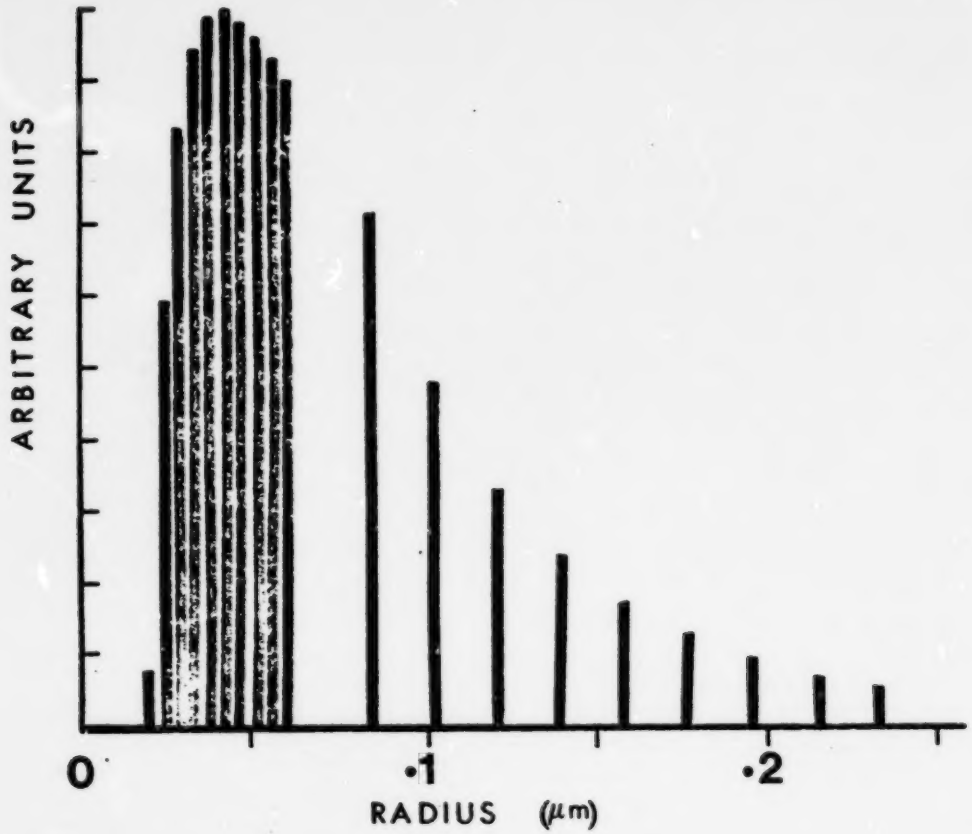
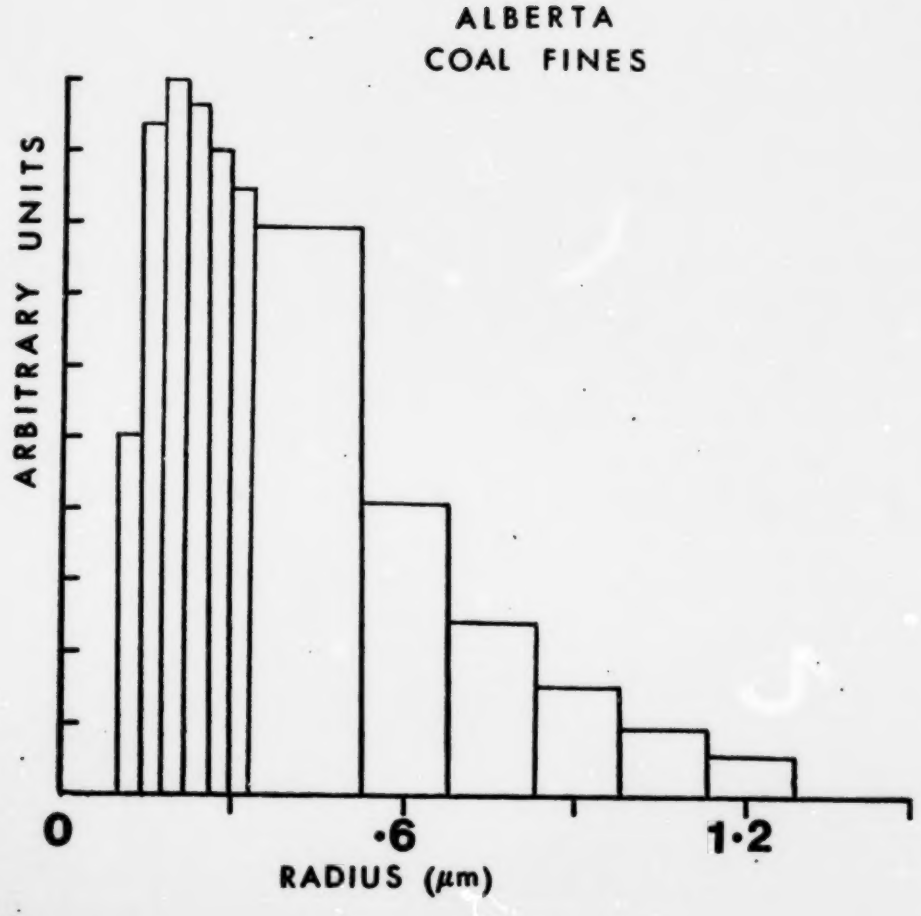

ARBITRARY UNITS
0
·1
·2
RADIUS (μm)

FIGURE 2. Size Distribution: Similar to figure (1) a histogram plot for 200 mesh size coal fines suspension in water from Alberta, Canada. The solution was allowed to settle for 24 hours and then filtered through a 8 μm millipore filter which yielded an average radius of 1.02 ± 0.53 μm.


ALBERTA
COAL FINES
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0
·6
1·2
RADIUS (μm)

this technique can yield excellent results as shown, optimum operation of the computer program required considerable skill and experience. We suggest that CRL not develop and use this technique until they have experienced QELS personnel available. Further the data quality required for this type of analysis is extremely high and is best done with newer generation correlators than are presently available at CRL. The Langley-Ford 1096 and the Malvern correlators give a measure of the data quality through a parameter called the 'background' ratio. Bad data functions due to a changing sample or due to drifting laser intensity can be spotted easily.

The determination of particle size in non-spherical particles is significantly more complex and involves incorporation of form factors into the analysis program. We have done this successfully for rod-like particles as part of another ongoing research program in our laboratory. If CRL in the future sees a need for this kind of data analysis then suitable arrangements can be made at that time.

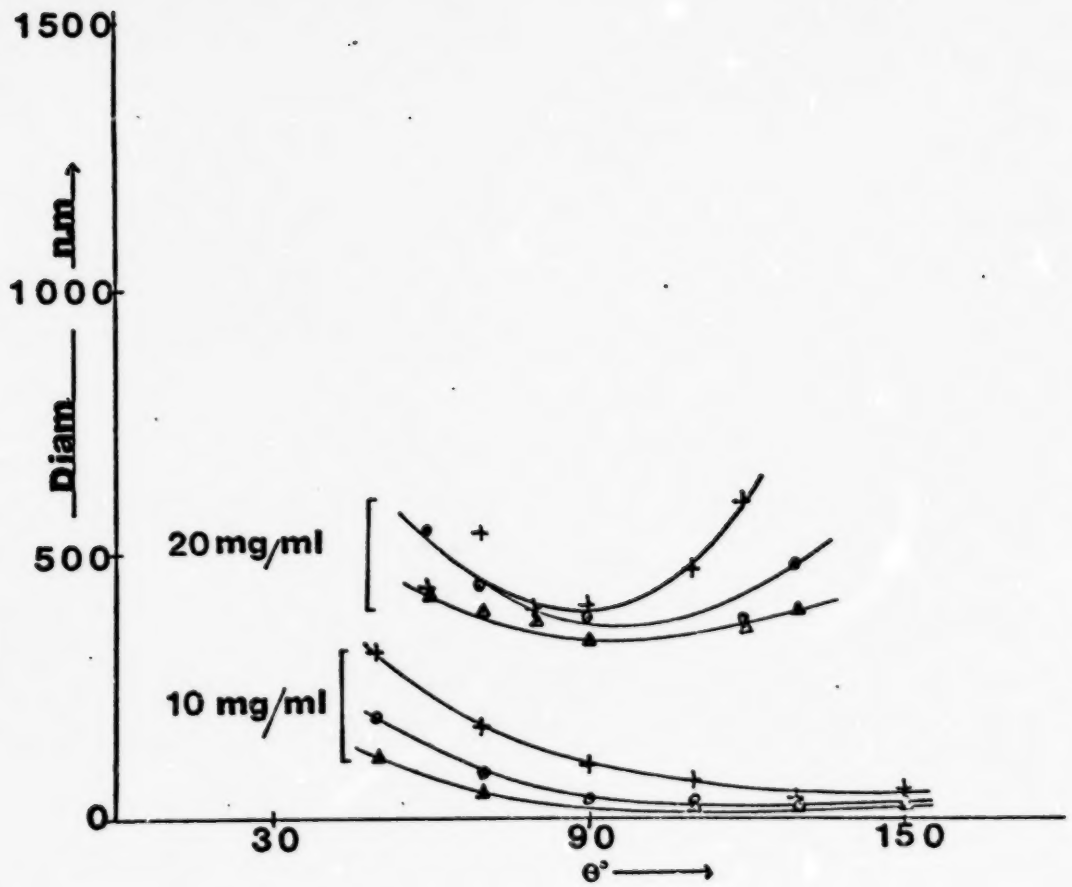
B) DETERMINATION OF THE HYDRODYNAMIC SIZE AND CONFIGURATION OF WATER SOLUBLE POLYMERS (INCLUDING POLYACRYLAMIDES) IN AQUEOUS SOLUTION AS WELL AS THE EFFECT OF VARIOUS IONS ON CONFIGURATION.

In the first part of this work QELS experiments were performed on samples of polyacrylamide and polyethylene oxide solutions in the concentration range of ~ 5 mg/ml - 20 mg/ml, as a function of scattering angle. The data was analyzed by both the cumulants method as well as the exponential sampling method. Experiments were also performed over periods ranging from hours to weeks to look for long time relaxation and degradation effects. Since no evidence of degradation was found most of the experiments

were performed within 24 hours from sample preparation. Of all the experiments conducted in the study these were the most difficult and least informative. This is due to several factors. When solutions of polymer were prepared using typical concentrations for flocculation the intensity of the scattered laser light was quite low leading to poor statistical reliability and a frustrating sensitivity to the presence of small amounts of dust in the sample. On the other hand if higher polymer concentrations were used the data was no longer analyzable because entanglements and interactions among the polymer molecules caused them to diffuse as groups or domains rather than as individual molecules. Hence data interpretation led to molecular sizes which were significantly larger than they should have been. These problems are demonstrated in Figure (3) which shows very complex and concentration dependent scaling curves. Prior to all these experiments we attempted to remove dust particles by centrifugation, but this was not entirely successful because of the tendency of the polymer molecules to coagulate and sediment along with the dust. While the data at 10 mg/ml is reasonably well behaved as a function of scattering angle, it demonstrates a bin time dependence characteristic of a very broad distribution of sizes. The data at 20 mg/ml yields poor scaling curves and hence we have no confidence in these results. This is not to say that there might be some interesting information present, but that a whole new theoretical model incorporating intanglements and interactions would have to be developed. This was clearly beyond the scope of this investigation. Hence this study was abandoned in favour of the labelling experiments which have much greater application to the flocculation process. These labelling

Figure 3. Size profiles:

The sizes of polyacrylamide flocullants for two separate concentrations as a function of scattering angle θ. The methods of cumulant was adopted to extract floc diameter in nanometers from QELS data. Each set of curves is plotted at three different bin times τ_1, τ_2 and τ_3 such that $\tau_1 < \tau_2 < \tau_3$.


1500
1000
500
0
Diam nm
20 mg/ml
10 mg/ml
30
90
150
θ°

experiments will be described in a subsequent section.

C) CONSTRUCTION OF A VARIABLE ANGLE LIGHT SCATTERING APPARATUS FOR DELIVERY TO CRL, EDMONTON.

The construction of the variable angle light scattering apparatus was completed during the summer of 1984 at which time it was shipped to CRL, Edmonton. Some delays in set-up occurred due to the move of CRL to a new building at Devon, but initial assembly and testing commenced in October 1984. During this and in subsquent testing in February 1985, intermittant defects in the quantum photometer became noticeable. The problem has been traced to a faulty amplifier/discriminator and a replacement has been obtained from the manufacturer. With this replacement, the system should be fully operational. As completed the apparatus consisted of a machined aluminum platform complete with adjustable positioners for laser mounting, a rotating arm centred on the optical axis and calibrated in degrees and tenths of degrees (on a vernier scale), a jacketed and thermally stable sample compartment with holders for standard 1 cm cuvettes, collection pinholes with mounts, a shutter assembly and a machined holder for the photomultiplier housing. Other related equipment such as temperature control equipment, detection electronics and laser are to be provided by the CRL.

D) LABELLING EXPERIMENTS: THE MEASUREMENT OF VISCOUS AND DIFFUSIONAL PROPERTIES OF PARTICLE/POLYMER SUSPENSIONS.

In this investigation the word 'labelling' refers to the use of QELS to monitor the diffusional properties of particles, such as latex spheres, coal fines or clay fines in solutions of polymers. While the pure polymer

solutions, as indicated in a previous section, were poor at scattering laser light this becomes a bonus for these experiments in that essentially all the scattered light comes from the particles. This allows one to monitor the motion of the particles only as the flocculation process proceeds. For reasons which will quickly become apparent a knowledge of the viscosity of the polymer solutions is vital for these studies. Hence, viscometric studies of these solutions are reported in this section.

THEORETICAL CONSIDERATIONS

In recent years, viscosity measurements of polymer solutions have been shown to be among the most informative of any physical experiment (see for example "The Physical Chemistry of Macromolecules" by Charles Tanford). In order to see the use of viscosity in several important relationships it is first useful to define a few terms quantitatively. If we use "n" to symbolize the viscosity of a polymer solution, then the relative viscosity of the solution (n_r) is,

$$n_r = n/n_o \qquad (1)$$

where n_o is the viscosity of the solvent alone. The value of the relative viscosity is that it can be written as a virial expansion of the volume fraction of the polymer ϕ.

$$n_r = 1 + \nu\phi + k\phi^2 + \ldots \qquad (2)$$

If the volume fraction is converted to a concentration through the expression

$$\phi = \nu c \qquad (3)$$

then equation (2) becomes

$$n_r = 1 + \nu\nu c + k\nu^2 c^2 \qquad (4)$$

The intrinsic viscosity [n] of a polymer is the coefficient of the single body term,

$$[n] = \nu v \qquad (5)$$

where v is the specific volume of the polymer and ν is the Einstein-Simha shape parameter (eg. 2.5 for spherical particles). The intrinsic viscosity is related to molecular properties of the polymer such as its molecular weight, whether it is branched or linear, whether it is a free draining or non-free draining random coil or whether it has a fixed particle shape such as a sphere or a rod.

The coefficient (k) of the two body term in equation (4) measures the extent of interaction between polymer molecules.

The main difficulty in performing accurate viscosity experiments in polymer solutions is that most viscometers require bulk flow. Therefore most experiments have to be done at a variety of shear rates so that results can be extrapolated to zero shear conditions. By using labelling experiments in which one follows the diffusion of particles of known size (eg latex spheres) one can conduct viscosity experiments at zero bulk shear. This is especially advantageous because the extrapolation process with all of its inherent uncertainties is no longer necessary. QELS spectroscopy measures the diffusion coefficients of the particles. Since the diffusion coefficient and the solution viscosity are inversely related then equation (4) can easily be converted to a form to input QELS results,

$$(D/D_o)^{-1} = 1 + [n]c + kv^2c^2 \qquad (6)$$

Now, however, one has to consider the fact that the solution is a three component system, solvent, polymer and particles. If one expands the

diffusion ratio (D/D_o) as a function of the polymer concentration then one obtains

$$(D/D_o)^{-1} = \text{const} + ([n]_p + k_{ps} v_p \phi_s) c_p + (k_p v_p^2) c_p^2 \quad (7)$$

In this expression, subscript p refers to a polymer quantity and subscript s refers to a particle quantity. Correspondingly, if one expands the diffusion ratio in terms of the particle concentration then,

$$(D/D_o)^{-1} = \text{const} + (2.5 v_s + k_{ps} v_s \phi_p) c_s + k_s v_s^2 c_s^2 \quad (8)$$

Since the specific volumes of both polymer and particles and the intrinsic viscosity of the polymer can be obtained independently then information on the remaining parameters can be obtained by fitting experimentally determined diffusion ratio vs concentration curves to simple second order polynomials. One parameter of key importance to flocculation is k_{ps} which measures the extent of interaction between the polymer molecules and the particles.

For this procedure to work properly the results must be independent of the particle size. This is because we are using the diffusion ratio in place of the relative viscosity and this is legitimate only if the particles sample the bulk viscosity.

RESULTS AND CONCLUSIONS

Although initial investigations used both polyethylene oxides and polyacrylamides we quickly learned that the latter system had a much larger

effect on the diffusion ratio. For this reason we concentrated on the polyacryamide systems, obtaining some samples from CRL, and some from Polysciences Inc. (Warrington, Pennsylvania). Later we received samples of a commercial flocculant 'Praestol' (Bayer Chemicals, Germany) which is also a large molecular weight polyacrylamide preparation obtainable in a range of anionicities. Figure (4) shows the initial diffusion ratio curves for these systems. The sharpest drop in diffusion ratio with polymer concentration was observed for the anionic Praestol sample (stars). The non-ionic Praestol system yielded a significantly smaller effect. The different molecular weight samples from Polysciences gave even smaller effects which were not always consistent. Studies which we will describe shortly show that the diffusion ratio curves are extremely sensitive to the presence of salt in the solution. Contamination of the solution by the salt in either the polymer or the particle stocks was shown to significantly reduce the slope of the curves. Since the Praestol system seemed to be the purest in this respect we used it as our principle system for study and analysis using the theoretical methods outlined above. Since quantitative fitting of equation (7) requires good quality data many carefully controlled experiments had to be performed on the latex sphere-Praestol solutions. Figure (5) shows some of this data and the corresponding polynomial fit to equation (7). The most interesting parameter which can be obtained from these fits is k_{ps} which measures the extent of interaction between the latex particles and the polyacrylamide molecules. The most heavily charged Praestol sample yielded a value of k_{ps} of about -8×10^4. Figure (6) shows how the fit value of k_{ps} varies as a function of anionicity over the available samples. There is clearly a very strong correlation between this

Figure 4: Diffusion ratio data for several polyacrylamide systems. (+ Polysciences M.Wt. 1 x 10^6; x Polysciences M.Wt. (5-6) x 10^6; ● Polysciences M.W.t 5 x 10^5; □ Praestol nonionic M.Wt. (4-6) x 10^6; * Praestol anionic M.Wt. (4-6) x 10^6

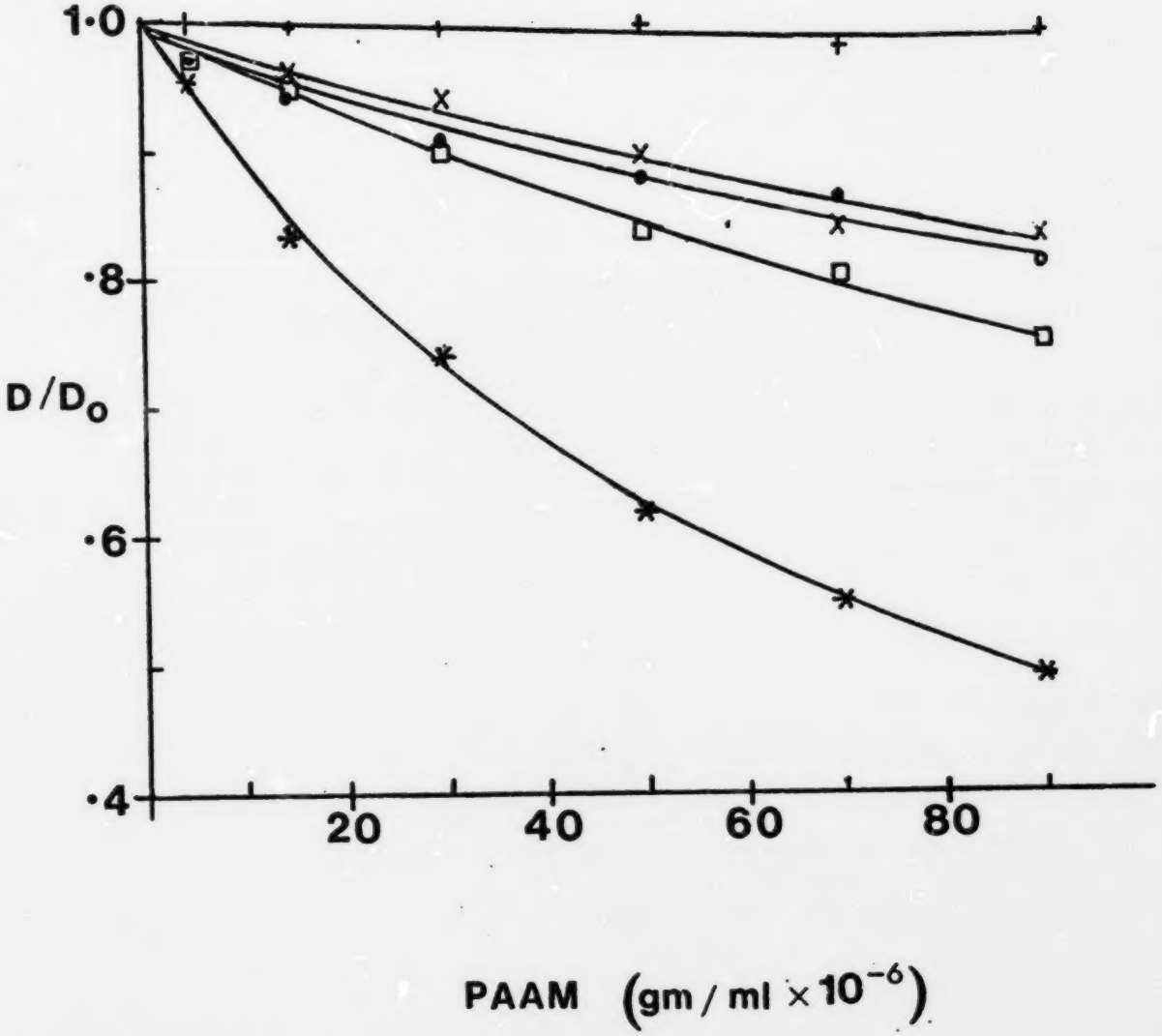

1·0
·8
·6
·4
D/D$_o$
20
40
60
80
PAAM (gm / ml × 10^{-6})

Figure 5: Diffusion ratio data and second-order polynomial fit for anionic praestol.

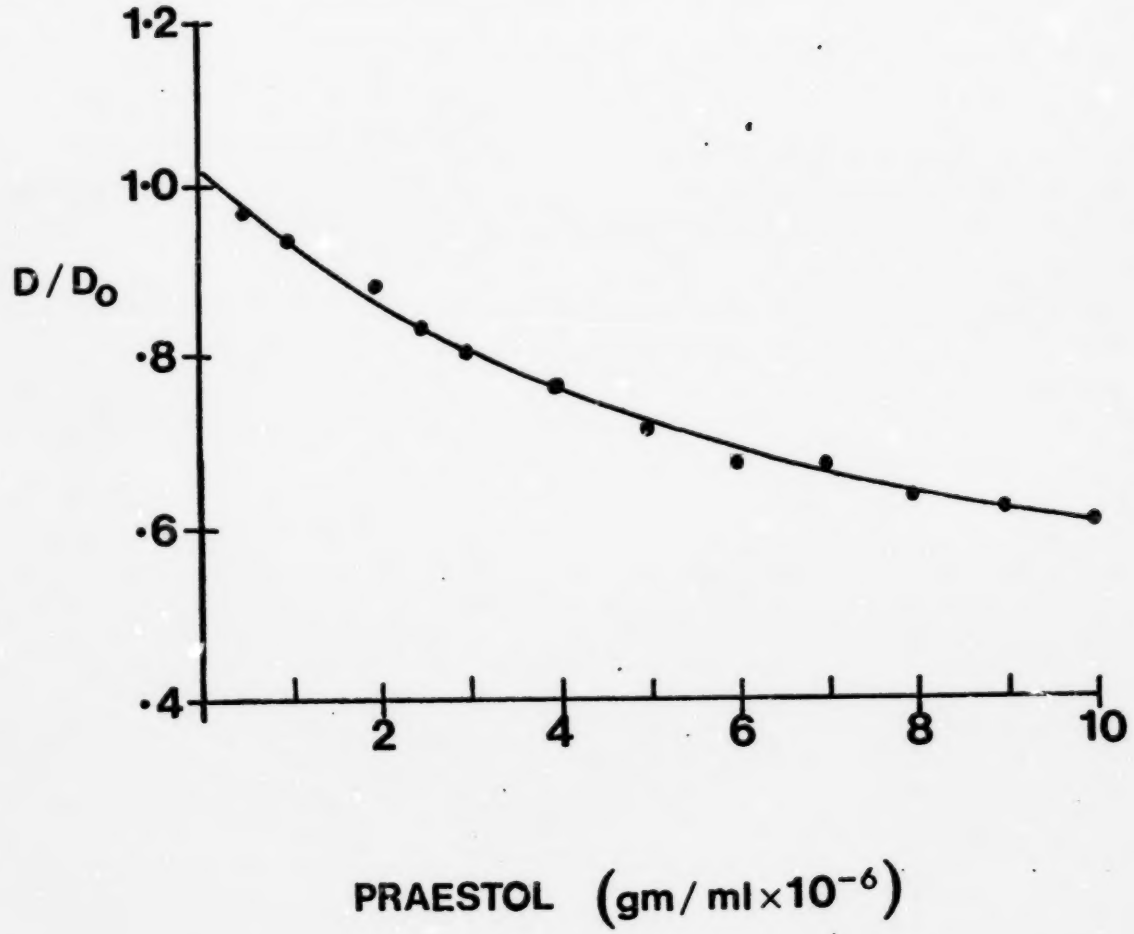

1·2
1·0
D / D₀
·8
·6
·4
2
4
6
8
10
PRAESTOL (gm / ml × 10⁻⁶)

FIGURE 6. Dependence of polymer surface charge on the particle-polymer interaction parameter.

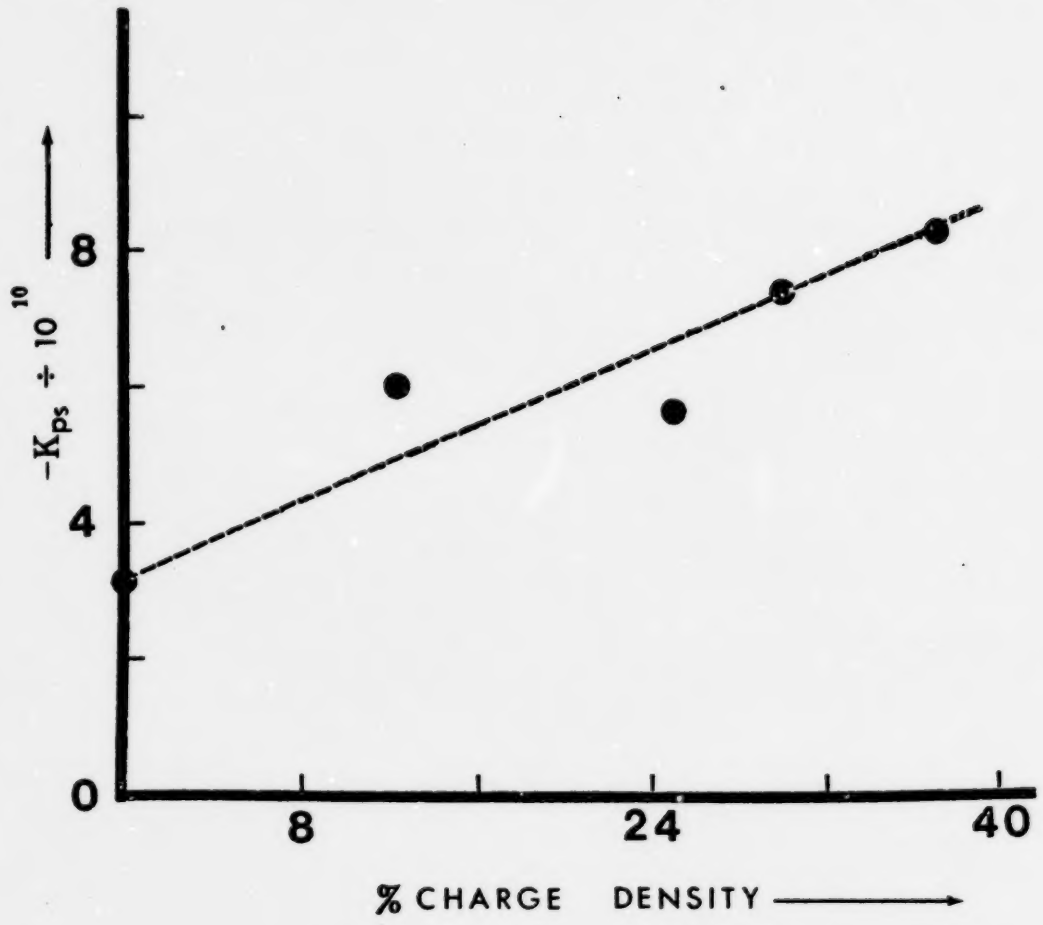
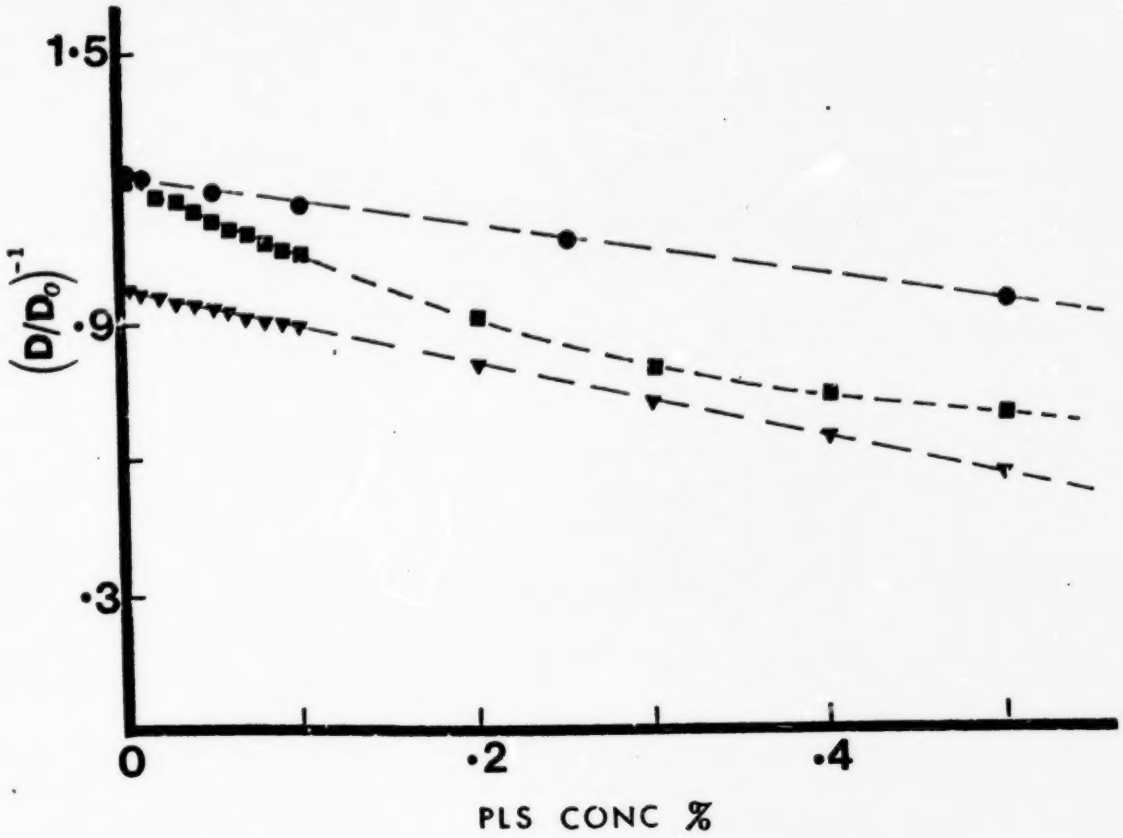

$-K_{ps} \div 10^{10}$
8
4
0
8
24
40
% CHARGE DENSITY

Figure 7: Diffusion ratio data plotted as a function of latex-sphere concentration. (▲ latex-spheres only; ■ latex spheres in 20 x 10^{-6} mg/ml Praestol (nonionic); ● dialyzed latex spheres in 20 x 10^{-6} mg/ml Praestol (nonionic))


1·5
·9
·3
$(D/D_0)^{-1}$
0
·2
·4
PLS CONC %

parameter and the charge on the polyacrylamide.

The value of the interaction parameter is, in principle, also available from a series of experiments in which the polymer concentration remains fixed, but the particle concentration is varied. Such a situation would correspond to the use of equation (8). At the beginning of these experiments we found that the behaviour of the diffusion ratio with increasing sphere concentration was poorly behaved. The difficulty was that the latex particles stock solution from the manufacturer contained significant amounts of salt. Hence at high particle concentrations this salt screened out the interactions and lead to much smaller changes in the diffusion ration than expected. By dialysing the latex spheres prior to mixing with the polymer a significant improvement was observed (see figure 7), but we are still not certain that all salt effects have been removed. Note that the diffusion ratio in figure (7) is inverted from that plotted in figure (6). The different trend in the curves is due to the different magnitude and sign of the other coefficient. A further analysis of these experiments will be available in a few months when Mr. Ansari's thesis is completed.

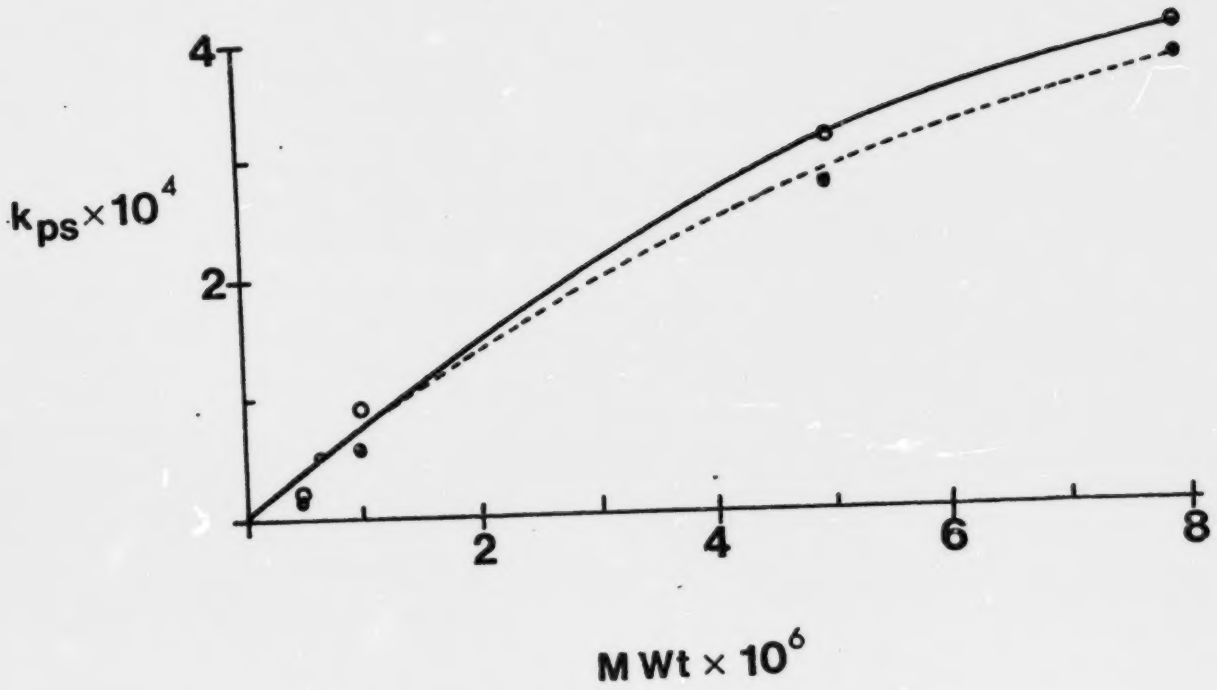
The last set of experiments which we report here refer to a measurement of the interaction parameter in a series of non-ionic polyacrylamides as a function of molecular weight. These involved measurement of the diffusion ratio as a function of polymer concentration and correspond therefore, to the use of equation (7) in the analysis. The results of this study are shown in figure (8) and demonstrate a consistent trend with molecular weight. The shape of this graph is suggestive that the interaction may be

directly related to the dimensions of the polymer, but this has not yet been confirmed. We are proceeding to examine the relation between the interaction parameter and the radius of gyration of the polymer.

It was mentioned earlier that the values of the coefficients obtained from diffusion ratio data should be independent of the size of the diffusing particle. This is because all particles, regardless of their size experience the same bulk viscosity. An indication that this holds quite well is shown by Figure (8). In practise this independence of particle size may not hold, but for reasons which do not jeopardize the original assumptions. For example one might find that the surface charge density varied from one size latex system to another. Indeed, such variation can occur between different lots of the same size latex particles although this has not been observed so far. Another reason is that the surface region of latex particles is known to have a less dense structure than internal regions. The relative amount of lower density may be a function of particle size leading to variation in the specific volume of the latex with size.

Although considerable work remains to fully develop the potential of QELS for studying the flocculation process we have certainly come a long way in the past two and a half years. It is clear that a parameter related to the extent of interaction between the flocculant polymer and the suspended particles can be routinely measured by light scattering. We have also shown that this interaction is primarily electrostatic since it increased linearly with the anionicity of the polymer. The true importance of the interaction parameter will depend on its ability to predict the success of potential flocculant in the industrial environment.

Figure 8: The interaction parameter K_{ps} is strongly dependent on the Molecular weight of the polyacrylamide polymer (● 0.261 μm latex spheres; o 1.1 μm latex spheres).


4
2
$k_{ps} \times 10^4$
2
4
6
8
M Wt × 10^6

Appendix I

Quasi-elastic Laser Light Scattering Study of Polymeric Flocculant Suspension

A paper presented at the International Symposium on Particulate and Multi-phase Processes. Miami Beach, Florida. April 1985

Quasi-Elastic Laser Light Scattering Study Of Polymeric Flocculant Suspensions

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INTRODUCTION

The phenomenon of flocculation (or coagulation in general) has been known to mankind for a very long time. Ancient Egyptians used it for making inks and dyes. Even today people in most of the third world countries make use of it to obtain clean drinking water by sparingly dissolving alum in water from rivers and lakes. However, its industrial use has been appreciated for only about a century.

With the modernization of the chemical industry came a wide variety of long chain high molecular weight synthetic polymers. Today these polymers are widely used as flocculating agents in industries such as coal and ore mining, pulp and paper, enhanced oil recovery, pharmaceuticals and water and waste water treatment. In particular the poly(acrylamide) polymers have been proven to be very economical, as only a fraction of a pound (0.005-0.01) of polymer can effectively flocculate a ton of coal washery effluent.

Some of the theories presented to unravel the mystery of flocculation processes include a bridging mechanism[1] between the suspended particles via the polymer chains, adsorption of polymer chains on clay particles[2], creation of localized electrical charged regions on the particle's surface, known as the electrostatic patch work model[3,4], a nonbridging, nonadsorptive, volume restriction mechanism[5] and network flocculation[6].

The experimental investigations conducted to seek a better understanding on the nature of flocculation are few in number. Turbidity measurements are frequently performed to assess the quality of a flocculating agent, but they provide no quantitative information on the interactions that take place between the polymer and the particle. While the bridging mechanism is quite popular, there has not been a strong effort to test it experimentally.

Our approach to the problem of flocculation is quite direct and quantitative, as we obtain information on the interactions between the suspended particles and the polymer via a dimensionless interaction parameter which is responsible for an

effective flocculation. We use the non-invasive technique of Quasi-Elastic Laser Light Scattering (QELS) to measure the interaction parameter by following the diffusion of suspended polystyrene spherical particles through aqueous solutions of polyacrylamide flocculants, polyacrylic acid and polyethylene oxide polymers. In this paper we only report the investigation on polyacrylamide flocculant suspensions because of their wide industrial application. The technique which we will describe here evolved from earlier investigations of electrostatic interactions in micelles[7], and of hindered diffusion of solid particles through solutions of dextran[8] and hyaluronic acid[9].

1. THEORETICAL CONSIDERATIONS

1.1 Quasi-Elastic Laser Light Scattering (QELS)

The theoretical and experimental basis for QELS is now well established. Several excellent books[10,11,12], reviews and papers are available on this subject. We will briefly describe only the pertinent features as applied to our system.

In homodyne QELS the scattered laser light intensity from the sample is autocorrelated in the time domain to yield the normalized intensity autocorrelation function

$$g^2(t) = \langle I(0)I(t)\rangle = 1 + B|g^1(t)|^2 \qquad (1)$$

where I(0) and I(t) are the scattered light intensities at time t=0 and at a later time t, respectively, and B is an experimental constant. The dynamical properties of the brownian particles in the scattering volume can be obtained through the electric field autocorrelation function, $g^1(t)$, where

$$g^1(t) = \frac{|\langle E^*(0)E(t)\rangle|}{|\langle E^*(0)E(0)\rangle|} = \exp[-2Dq^2t] \qquad (2)$$

In this expression E is the electric field intensity and E^* is its complex conjugate, D is the translational mutual diffusion coefficient and q is the scattering vector ($q = 4\Pi n.\mathrm{Sin}(\theta/2)/\lambda$); n being the refractive index of the solution, λ is the wavelength of the incident laser light and θ is the scattering angle.

The translational diffusion coefficient D of a particle is related to its frictional coefficient f_r via the Stoke's-Einstein equation :

$$D = kT / f_r = kT / 6\Pi\eta r \qquad (3)$$

where kT, η, and r are the thermal energy of the system, the coefficient of viscosity of the solution and the hydrodynamic radius of the diffusing particles respectively.

Particle sizes can be determined from this equation but only in the limit of infinite dilution.

1.2 Particle-Polymer Interactions & Flocculation

In recent years, viscosity measurements of polymer solutions have been shown to be among the most informative of any physical experiment[13]. The relative viscosity can be written as a virial expansion of the volume fraction of the polymer,

$$\frac{\eta}{\eta_o} = \eta_r = 1 + \nu\phi + K\phi^2 + \ldots\ldots \qquad (4)$$

If the volume fraction is converted to a concentration, C , through the expression

$$\phi = VC \qquad (5)$$

then equation (4) becomes

$$\eta_r = 1 + \nu VC + KV^2C^2 \qquad (6)$$

The intrinsic viscosity $[\eta]$ of a polymer is the coefficient of the single-body term,

$$[\eta] = \nu V \qquad (7)$$

where V is the specific volume of the polymer (taken to be 0.7 from an earlier paper[14]) and ν is the Einstein-Simha shape parameter. The intrinsic viscosity is related to molecular properties of the polymer such as its molecular weight and end to end distance through the following equation[15],

$$[\eta] = \Phi_c \langle r^2 \rangle^{3/2} / M \qquad (8)$$

In this equation $\Phi_c = 2.1 \times 10^{23}$, is a universal constant. If $[\eta]$ is taken in units of $cm^3 gm^{-1}$ and the end to end distance, $\langle r^2 \rangle^{3/2}$, is in units of cm^3, then the end to end distance is related to the radius of gyration , $\langle R_g^2 \rangle$, as

$$\langle R_g^2 \rangle = \langle r^2 \rangle / 6 \qquad (9)$$

Equation (8) can be applied to linear and branched polymers, even if they have a fixed particle shape such as a sphere or a rod, in both free-draining and non-free-draining coil approximations. The coefficient (K) of the two-body term in equation (6) measures the extent of interaction between polymer molecules.

The main difficulty in performing accurate viscosity experiments in polymer solutions is that most viscometers require bulk flow. Therefore, most experiments have to be done at a variety of shear rates so that results can be extrapolated to zero shear conditions. By performing experiments using QELS in which one follows the diffusion of particles of known size (eg latex spheres), one can conduct viscosity experiments at zero bulk shear. This is specially advantageous because the extrapolation process with all of its inherent uncertainties is no longer necessary. Since the diffusion coefficient and the viscosity are

inversely related, through equation (3), then equation (6) can easily be converted to a form to input QELS results,

$$(D/D_o)^{-1} = 1 + [\eta]C + KV^2C^2 \qquad (10)$$

Now, however, one has to consider the fact that the solution is a three-component system, solvent, polymer and particles. If one expands this diffusion ratio as a function of the polymer concentration then one obtains

$$(D/D_o)^{-1} = \chi + ([\eta]_p + K_{ps}V_p\phi_s)C_p + (K_pV_p^2)C_p^2 \qquad (11)$$

In this expression, χ, refers to a constant term and the subscripts "p" and "s" refer to a polymer and a particle quantity, respectively.

Since the specific volumes of both polymer and particles and the intrinsic viscosity of the polymer can be obtained independently, information on the remaining parameters can be obtained by fitting experimentally determined diffusion ratio to concentration curves using simple second order-polynomials. One parameter of key importance to flocculation is K_{ps}, which measures the extent of interaction between the polymer molecules and the particles.

For this procedure to work properly the results must be independent of the particle size, since the use of the diffusion ratio in place of the relative viscosity is legitimate only if the particles sample the bulk viscosity.

2. EXPERIMENTAL TECHNIQUES

2.1 QELS Experiments:

The main features of our QELS experimental setup are presented in figure (1). A vertically polarized continuous beam of laser light was passed through the glass cuvette containing the solution which scattered this light. This cuvette was placed in a temperature controlled cylinderical sample holder, containing water. The unscattered main beam was captured by a beam trap to avoid stray light. The main laser source employed in this study was a He-Ne (Jodon Manufacturing Ltd. Michigan) laser, λ = 632.8 nm, with a power of 0.15 mw. The scattered light was collected by a photomultiplier (PMT) tube (RCA 8852) after it passed through two pin holes A1 and A2, 400 μm in diameter, which defined the scattering volume and the coherence area on the PMT surface. The PMT was mounted on a rotatable arm scanning a scattering angle of 0 to 160 degrees. The PMT output is proportional to the scattering intensity and fluctuates on a characteristic inverse time scale ($\Gamma = Dq^2$). The output pulses were then passed through an amlifier-discriminator system (model 1140 Quantum photometer, Princeton Applied Research Corp, Princeton, N.J., USA). A correlator (model 1096 Langley-Ford Co, Mass, USA) was employed to yield auto-correlation functions according to equation (1). A pulse counter (model 8010, Dana Corp., USA) was employed to monitor the count rates. The final data acquisition and analysis was done on an IBM XT microcomputer.

Our QELS spectrometer provides rapid measurements of D for mono disperse spherical polystyrene particles (< 1 minute at a concentration of 0.0001 % solids) within 5 % accuracy. All the experiments were carried out at a temperature of 21 ± 0.5°C, and a scattering angle of 90°.

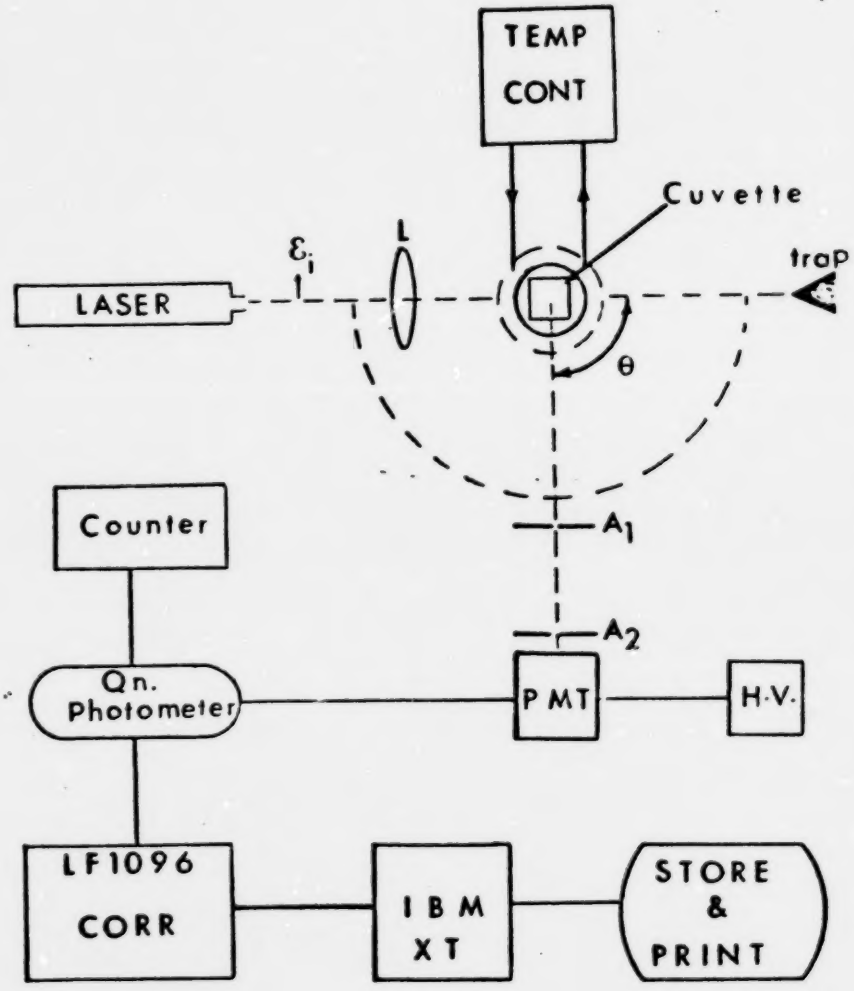

FIGURE 1. QELS SYSTEM: Schematic diagram of Quasi-Elastic Laser Light Scattering Experiment.

2.2 Particle Size Analysis

For polydisperse systems we used either the method of cumulants[16] or the method of exponential sampling[17]. The first of these methods is simple and normally yields the first two moments of the distribution G(Γ). These moments yield the average particle size or the average diffusion coefficient and the variance of the distribution, respectively. For a monodisperse sample all higher moments vanish and the first cumulant yields an average diffusion coefficient <D>. When applied to a distribution of scatterers,

equation (1) becomes

$$g^2(t) - 1 = B \left(\int_0^{\infty} \exp\{-\Gamma t\}\, G(\Gamma) d\Gamma \right) \qquad (12)$$

he exponential sampling technique describes a numerical method to invert the Laplace transform in this equation. One of us (FRH) has applied this technique in our laboratory to obtain histograms of size distributions.

Such a histogram of the size distribution for a polystyrene latex particle suspension, with a nominal diameter of 261 nm, in water is presented in figure (2). Another similar histogram for a coal suspension of 200 mesh size from Alberta, Canada is shown in figure (3). This suspension was allowed to settle overnight. These histogram plots indicate narrow size distributions for our systems of interest. Hence for further work regular data analysis employed the method of cumulants.

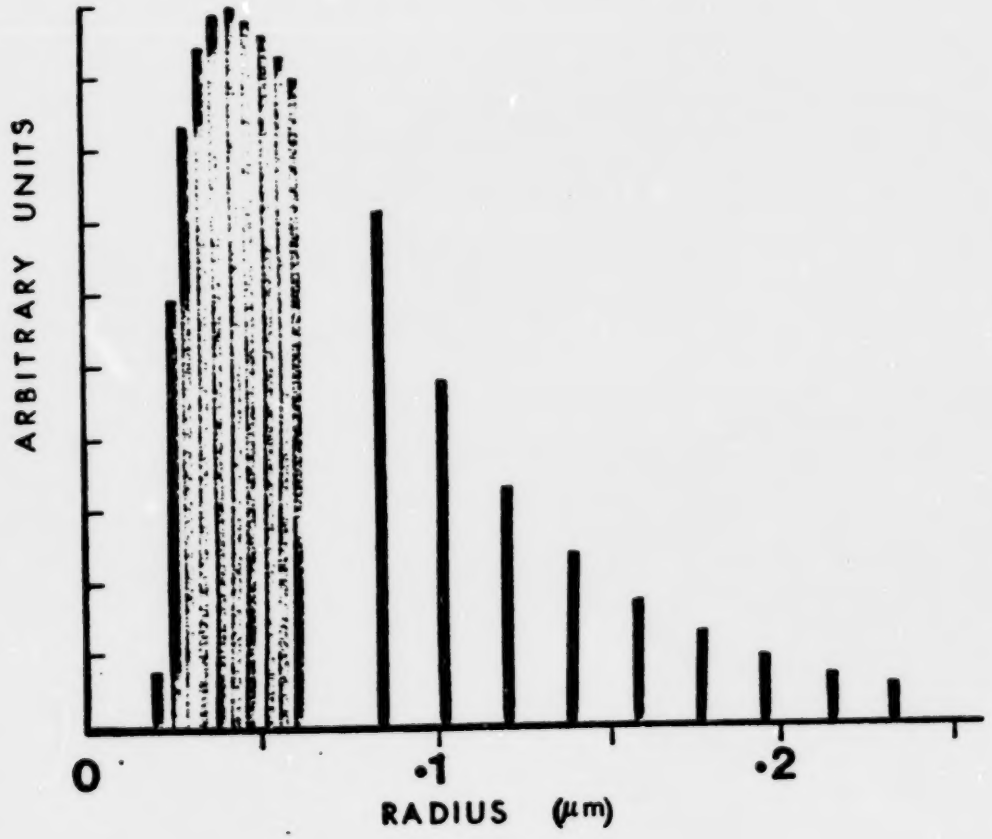

FIGURE 2. Size Distribution: Histogram plot, using the exponential sampling technique (equation 12), for polystyrene spherical particles. This analysis yields an average radius of 0.173 ± 0.1 μm, while an average value of 0.130 ± 0.05 μm was obtained from electron microscopy. The particles were suspended in water as 0.001 % solids.

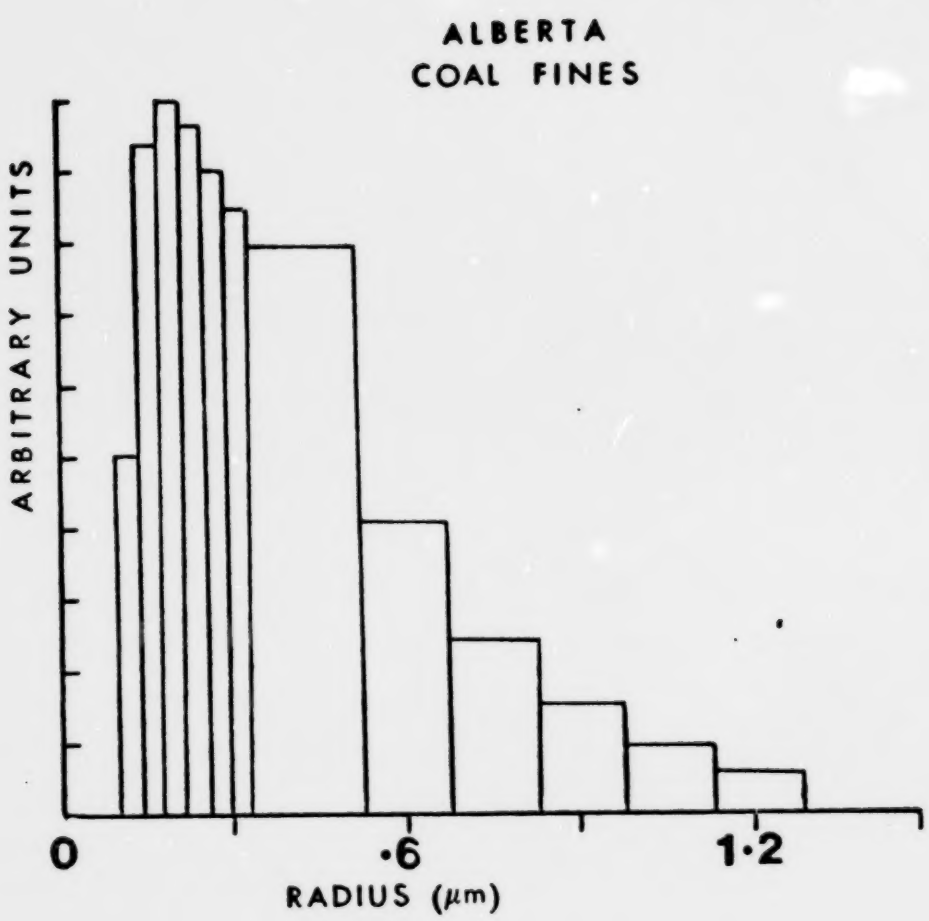

FIGURE 3. Size Distribution: Similar to figure (2) a histogram plot for 200 mesh size coal fines suspension in water from Alberta, Canada. The solution was allowed to settle for 24 hours and then filtered through a 8 μm millipore filter which yielded an average radius of 1.02 ± 0.53 μm.

2.3 Rheology Experiments

Rheology experiments were carried out to characterize the polymer sample by measuring their intrinsic viscosities. A cone-plate micro viscometer (Brookfield Engineering Inc. Mass, USA) with 0.8^{o} cone was employed for these measurements. All measurements were performed at $21^{o}C$ at a shear rate range of 4.50 to 450 sec^{-1}. These measurements were then extrapolated to zero shear rates to obtain zero-shear bulk viscosity of the polymer solution.

2.4 Sample Preparation

The non-availability of polyacrylamide (PAM) samples having a range of molecular weights from a single manufacturer was a serious problem. For this reason these samples were collected through various sources.

Laboratory grade samples of non-ionic PAM of Mwt 5 X 10^5, 1 X10^6, and 5 X 10^6 were obtained from Polysciences Inc (Warrington, Pa, USA). Industrial non-ionic PAM flocculant of Mwt (4-5 X 10^6) and three other preparations of the same Mwt but different charge densities (12.5 %, 25 %, & 37 %) were kindly supplied by the Coal Research Lab (Energy Mines & Resources Canada, Devon, Alberta). Two more samples, one non-ionic and an anionic (30 %), were kindly supplied as a gift by Dow Chemical Co (Sarnia, Ontario, Canada).

For QELS and rheology experiments the samples were made by dissolving PAM in doubly distilled deionized water. Stock solutions of 1 % (w/v) were made from smaller Mwt PAM (Polysciences samples) and 0.1 % (w/v) solutions were made from all other samples, as the higher Mwt samples tend to form highly viscous gel-like structures at higher concentrations. These stocks were allowed to equilibrate overnight but the final solutions, of concentration ranging 0% to 0.01% (0-100ppm), were used within 24 hours.

Polystyrene latex spheres (PLS) employed as our model particles were obtained from Dow Chemical Co (Seragen Inc, Indianapolis, Indiana, USA) and Duke Scientific Co (Palo Alto, California, USA) in a size range of 0.087 to 1.1 μm having a concentration of 10 % solids. These suspensions were further diluted using doubly distilled deionized water. Concentrations of 0.005 % solids were employed in this experiment.

Finally the PLS particles were added to solutions of PAM, shaken well, and allowed to settle for about ten minutes before every QELS diffusion run.

3. RESULTS AND CONCLUSIONS:

Good quality data was obtained through many carefully controlled QELS experiments performed on the model PLS-PAM solutions. Figure (4) shows some of this data, employing PAM and PLS of varying molecular weights and sizes, respectively, and the corresponding polynomial fit to equation (11). The most interesting parameter which is obtained through these fits is K_{ps} which measures the extent of interaction between the PLS particles and the PAM molecules. We also see that there is no consistent effect of particle size on these (D/D_o) curves.

The polymer size dependence in these graphs suggests that the interaction may be directly related to the dimensions of the polymer. This relationship is confirmed in figure (5) where K_{ps} is plotted against the radius of gyration, $\langle R_g^2 \rangle$, of the PAM polymer molecule. The $\langle R_g^2 \rangle$ values were obtained through equation(8).

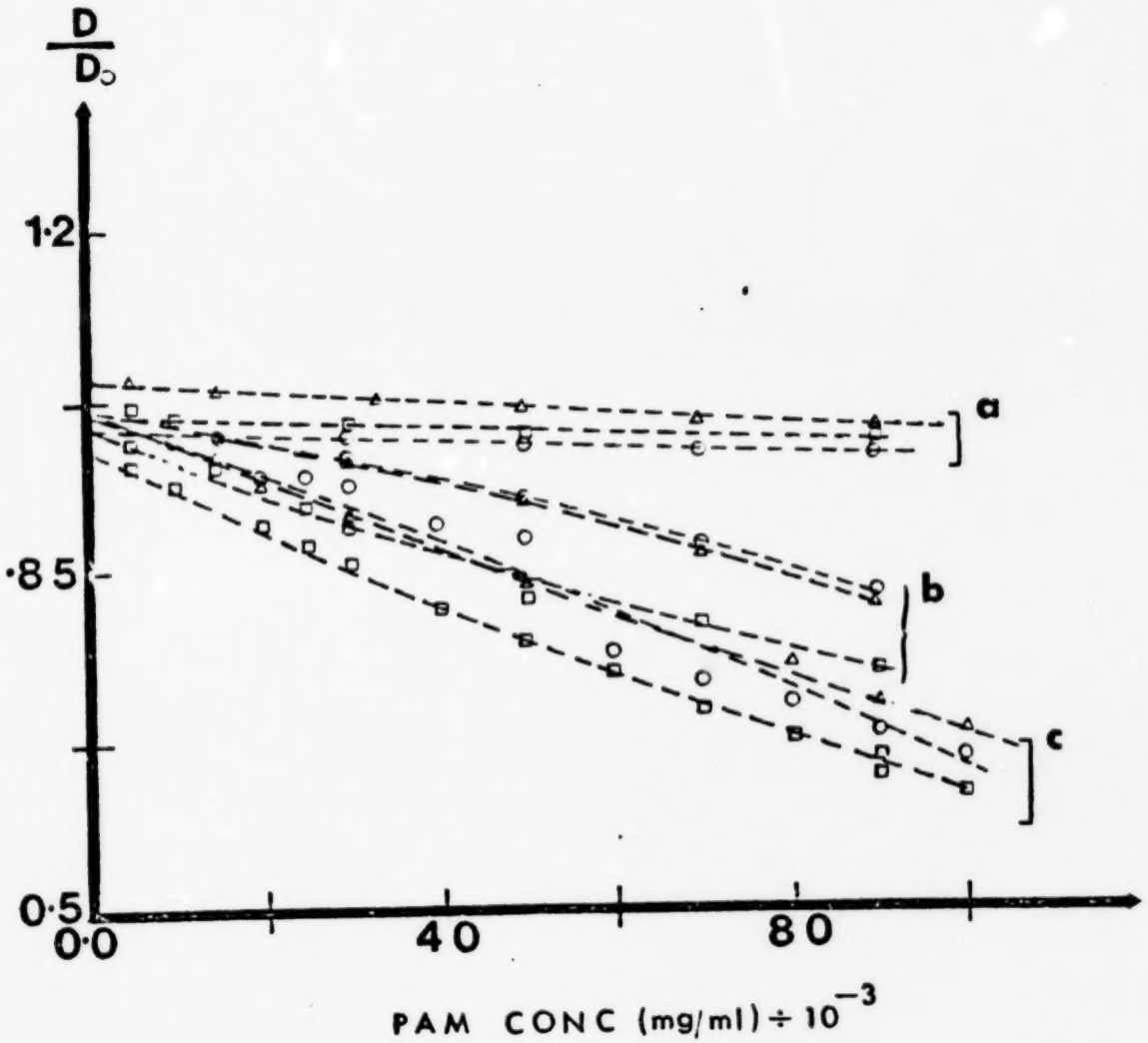

FIGURE 4. Particle diffusion ratio: Each set of curves a, b and c represent diffusion data on aqueous suspensions of non-ionic polyacrylamide polymers of molecular weight 1, 4-5 and 6-8 million, respectively. The following symbols are used to denote the diffusing polystyrene latex particles through these suspensions: △ : 0.500 μm, □ : 1.1 μm and ○ : 0.261 μm. The dashed curves are the polynomial fits to equation (11). The effect of reducing particle diffusion by an increase in polymer molecular weight is clearly evident. D and D_o are the diffusion coefficients of PLS particles at some polymer concentration and at zero polymer concentration, respectively.

The influence of polymer surface charge on the particle-polymer interaction parameter was studied by employing PAM samples of varying surface charge densities. Figure (6) represents initial (D/D_o) curves plotted against the concentration for two anionic PAM samples. This data suggests a weak, but consistent, dependence on particle size. However, this dependence is approximately of the same order of magnitude as that of the experimental errors involved in these measurements except for

0.091μm and 1.1 μm PLS particles in 12.5 % PAM {Mwt.(4-5) x 10^6} and 30 % PAM {Mwt. (6-8) x 10^6 } anionic solutions, respectively. This dependence can be attributed to the presence of varying degrees of small quantities of inorganic salts (0.2 %) and a surfactant (0.1 to 0.5 %) in the PLS preparations.

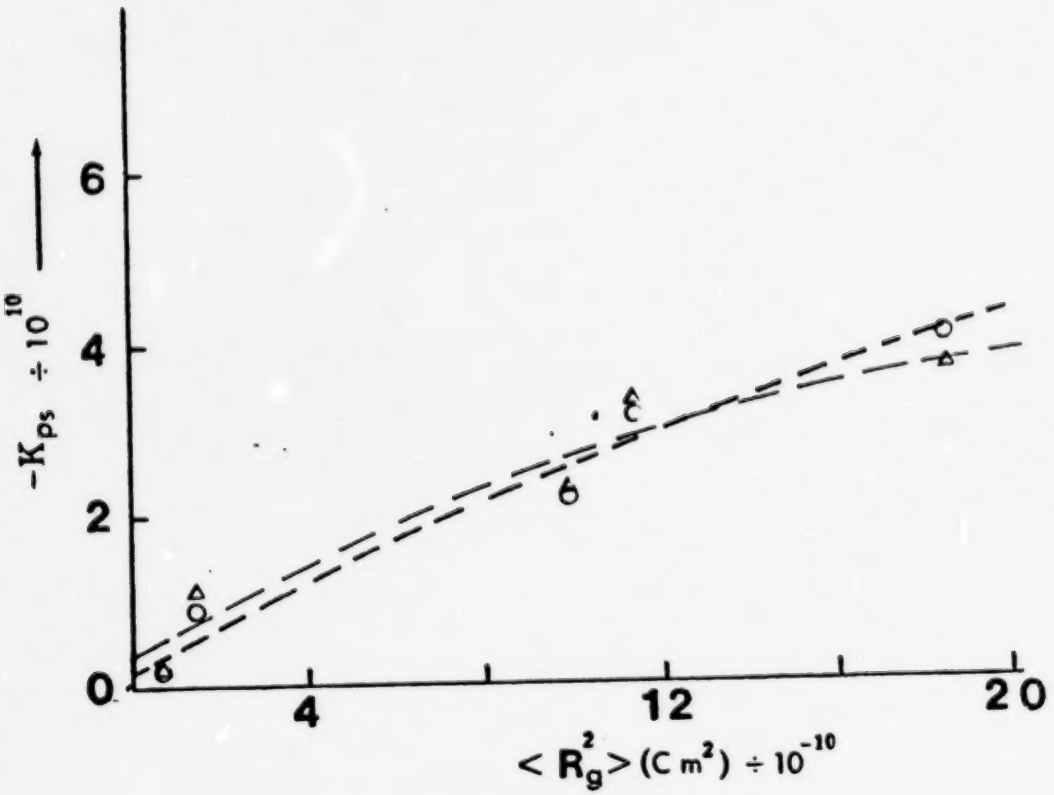

FIGURE 5. Particle-Polymer interaction and flocculation. The dependence of particle-polymer dimensionless interaction parameter, K_{ps}, on the polymer chain dimensions given by its radius of gyration, $\langle R_g^2 \rangle$. K_{ps} is obtained from the diffusion data of figure (4) and $\langle R_g^2 \rangle$ is calculated through equation (8). Dashed curves are the least squared fits to the calculated K_{ps} values for the PLS particles of sizes 0.261 μm (Δ) and 1.1 μm (o) respectively.

A stronger effect on (D/D_o) slope is noticeable while using the anionic PAM solutions (figure 6) compared with their non-ionic counterparts (figure 4) in the same molecular weight and concentration regimes. Hence one would expect larger values for the particle-polymer interaction parameter, K_{ps} , and therefore a much stronger flocculation effect. This is shown in figure (7).

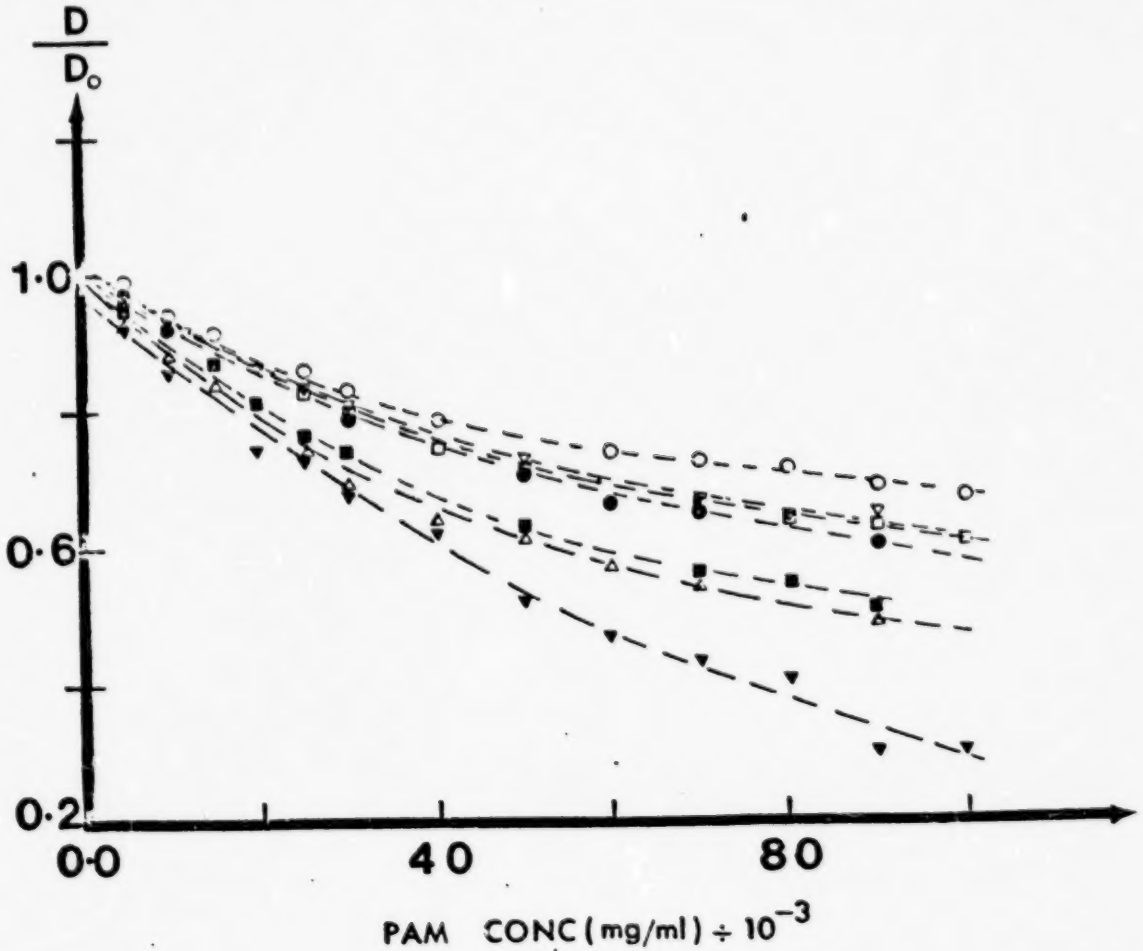

FIGURE 6. Particle diffusion ratio for two anionic PAM of molecular weights of 4-5 million (25 % anionic) and 6-8 million (30 % anionic). The symbols used here for the diffusing particles are as follows:

4-5 million PAM, ▽ = 0.261 μm, ● = 0.500 μm, △ = 1.1 μm
6-8 million PAM, ○ = 0.091 μm, □ = 0.261 μm, ■ = 0.500 μm, ▼ = 1.1 μm

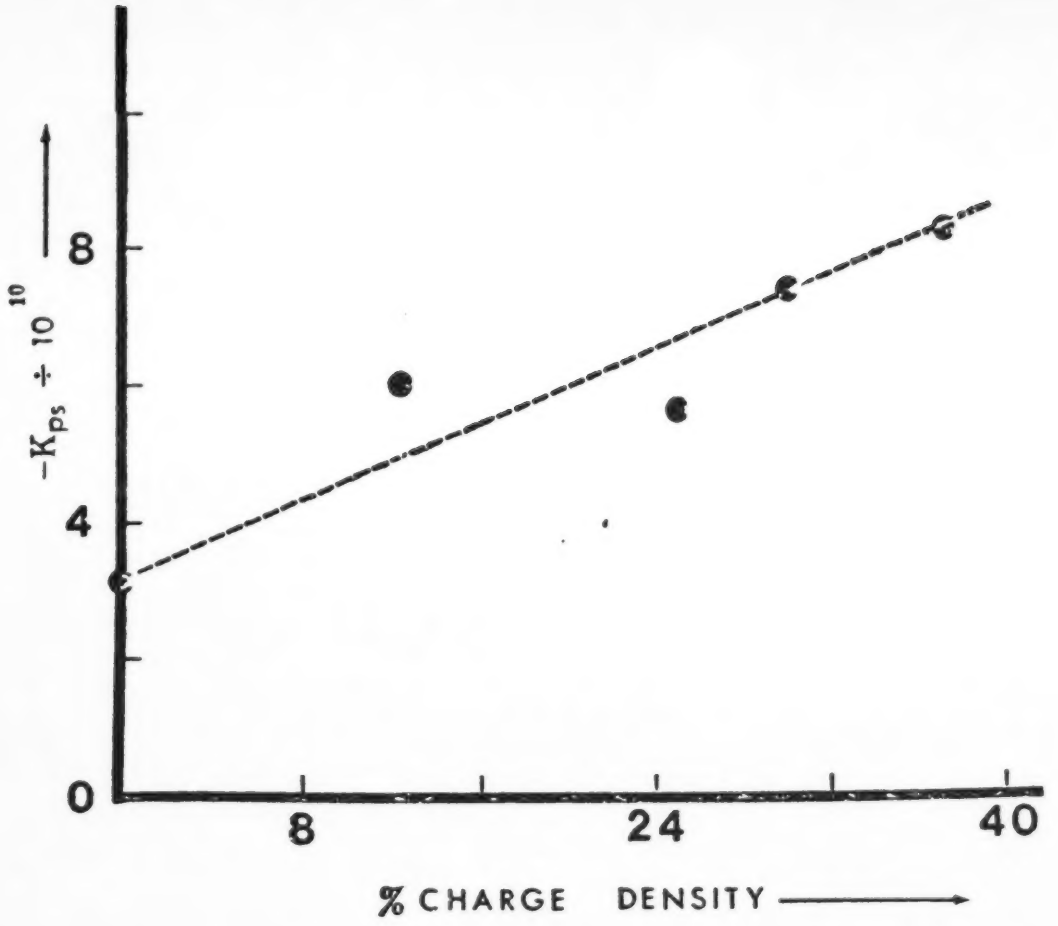

FIGURE 7. Dependence of polymer surface charge on the particle-polymer interaction parameter.

This figure clearly shows a very strong correlation between K_{ps} and the charge on the polymer (PAM) molecule. This correlation may be at least partly attributable to the elongation of the polymer chain due to the electrostatic repulsions among the neighbouring charged groups present along the chain.

A preliminary error analysis shows that the major contribution to the errors involved in the determination of K_{ps} comes from the intrinsic viscosity, $[\eta]$, measurements. These errors, mainly because of extrapolations as described in section (1.2), are estimated to be between 15 to 20 % . The instrumental uncertainties in these measurements are between 5 to 10 % . According to these preliminary estimates the error on the K_{ps} values is found to be about 15 to 20%.

5. SUMMARY

We present a straight forward, direct and quantitative approach, to the study of polymeric floculation by applying the technique Quasi-Elastic Laser Light Scattering. This study yields the extent of interactions between the particles and polymer molecules in a flocculation process. These interactions are measured experimentally by determining a dimensionless parameter, K_{ps} . We find this particle-polymer interaction parameter to be dependent upon the dimensions and surface charge of the polymer, and independent of the particle size. On the application side we conclude that our technique provides a new means for monitoring the flocculation processes. The technique may provide an improved process control, since the effectiveness of different kinds of flocculants widely used in various industries, can be rapidly and accurately tested. Optimum conditions for flocculation such as dose rates, the nature of the polymer including size and charge can be easily determined. Finally the determination of the particle-polymer interaction parameter, K_{ps} for a variety of systems may lead to refinements in the theories of flocculation.

We are continuing our investigation to obtain particle-polymer, particle-particle and polymer-polymer interaction parameters using the same experimental techniques but are employing a slightly different approach in expanding the particle diffusion ratio in terms of the particle concentration as opposed to polymer concentration discussed in this paper. The complementary technique of electron microscopy in both transverse and scanning modes will also be used. However this will be reported elsewhere.

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